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National Performance Audit Program 1979 Proficiency Surveys for Sulfur Dioxide Nitrogen Dioxide, Carbon Monoxide, Sulfate Nitrate, Lead and High Volume Flow

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16. ABSTRACT

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The various sample materials are monitored by the Quality Assurance Division to assure that samples are stable, of uniform composition and are representative of pollutant concentration levels encountered under field sampling conditions and that all materials conform to prescribed standards of accuracy. Sample materials are required to be similar enough to true air pollution matrices not to introduce unrealistic conditions of sample preparation or impose handling techniques that are not a part of the normal monitoring and analytical activity.

A major survey objective is the assessment of routine analytical performance. After results are evaluated by the Quality Assurance Division, an individual report is promptly returned to each participant. This report contains a summary of survey results for the year 1979.

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1979 PROFICIENCY SURVEYS

FOR

SULFUR DIOXIDE, NITROGEN DIOXIDE, CARBON MONOXIDE, SULFATE, NITRATE, LEAD AND HIGH VOLUME FLOW

by

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ABSTRACT

The Quality Assurance Division of the Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, administers semiannual Surveys of Analytical Proficiency for sulfur dioxide, nitrogen dioxide, carbon monoxide, sulfate, nitrate, and lead. Sample material, simulating ambient air pollution samples as closely as possible, are furnished to participating laboratories. Surveys of hi-vol sample flow are conducted annually using a modified orifice.

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A major survey objective is the assessment of routine analytical performance. After results are evaluated by the Quality Assurance Division, an individual report is promptly returned to each participant. This report contains a summary of survey results for the year 1979.

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SECTION I
INTRODUCTION

The 1979 Proficiency Surveys continue the regular surveys by the Environmental Monitoring Systems Laboratory (EMSL) of agencies which routinely collect and analyze ambient air samples. Sample materials, furnished by EPA for this purpose are designed to simulate as closely as possible several types of collected air pollution samples. It is prudent to note that these samples treat only the analytical portion of the total air monitoring capability, and do not deal with errors from sample collection, transportation, handling, storage, and data processing. Rankings in the surveys, except as may occasionally be due to unpropitious circumstances, reflect the effectiveness of internal quality assurance programs.

The Proficiency Surveys allow EPA to monitor the caliber of air pollution analyses, and permit the participating agencies to assess their own performances vis-a-vis their peers.

With the assistance and cooperation of the EPA Regional Offices, the surveys are conducted by the Quality Assurance Division (QAD)/EMSL, Environmental Research Center, Research Triangle Park, North Carolina 27711. Inquiries and applications to participate should be directed to that address. Included in this report is a discussion of the program, description of the survey materials, statistical summaries and the results.

SECTION 2
PROGRAM PROFILE

Participants in the surveys are solicited by the Regional Quality Control Coordinator in each of the ten Regions. Once a laboratory enrolls in a survey for a particular pollutant, it is automatically notified of subsequent surveys for that pollutant. Participants are assigned an identifying code number which remains in effect for all surveys. Included in the surveys are representatives of federal, state, local, industrial and foreign air pollution monitoring agencies.

Soon after a roster is established, instructional information and blind sample materials are mailed. Surveys are presently conducted twice a year for carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), lead (Pb) on filter strips, sulfate ($SO_4^{=}$) and nitrate (NO_3^{-}) on filter strips and once a year for hi-vol flow. Reports now indicate the reported value and include an historical frequency distribution of test results. A comprehensive report is prepared yearly summarizing the survey results of that year.

Laboratories submitting abnormal measurements are offered an opportunity to analyze another set of unknown samples, similar to those of the main survey, but of different concentrations. However, the retest results are not included in this report.

SECTION 3
STATISTICAL CONSIDERATIONS

Before 1979, the surveys gave target and sample ranges that defined the sphere of all creditable results. Under the former system, results falling within the sample range indicated a fine analytical job and those within the wider target range a respectably good one. This format enjoyed wide favor, due to the clear, explicit and uncontestable tableau it presented for scoring any single test result.

Beginning with the 1979 survey year, in an effort to enable scoring of individual results, a new format is used which presents cumulative frequency distributions of the results of earlier surveys.

Investigators have long agonized over which measurements are totally believable and which are wholly discreditable. Judgment of the investigator was the historical criterion for rejection of data. David Bernoulli, writing in an earlier century about astronomical observations[1], stated that he could see no way of drawing a dividing line between data values that are to be utterly rejected and those that are to be entirely retained. A fair and dispassionate system for judging outliers is needed in any survey.

The criterion chosen for the 1979 surveys is one that has been in use for a long time, the Chauvenet's Criterion.[2] This criterion is based on the normal distribution and advises rejection of an extreme observation if the probability of occurrence of such deviation from the mean of the n measurements is less than 1/2n. Since inclusion of spurious data vitiates test results by biasing both the survey mean and precison, but removal of good measurements merely excludes some of the data[3], it is thought that it is better to reject some good data than to include truly anomalous measurements.

Several of the statistical procedures used to evaluate survey results are reviewed below. The F test, t test and an extension of the analysis of variance. The F test was used to test whether the variance of one test method exceeded that of another. The ratio of the variances was not expected to exceed a critical value, which is based on the number of observations (measurements) in each test method, unless differences exist in the precision of the two methods. If F equals one, there is no difference in variability between the two methods. Values less than one have no meaning. The value of the statistic F is given by the expression:[4]

$$F = s_1^2/s_2^2 \qquad \text{(Eq. 1)}$$

where:

s_1 = standard deviation of method 1

s_2 = standard deviation of method 2

Two assumptions that underlie the use of the t test for comparing the means of two samples are that their population distributions are normal and that their population variances are equal.[4] When those conditions are satisfied, the variance estimates can be pooled and the statistical relations shown below are assumed to apply. The pooled variance is given by the following equation:

$$s_p^2 \text{ (pooled)} = \frac{(N_1 - 1)s_1^2 + (N_2 - 1)s_2^2}{N_1 + N_2 + 2} \qquad \text{(Eq. 2)}$$

The standard error of the difference between the mean is given by the equation:

$$s_d = \sqrt{\frac{(N_1 - 1)s_1^2 + (N_2 - 1)s_2^2}{N_1 + N_2 - 2}} \sqrt{\frac{1}{N_1} + \frac{1}{N_2}} \qquad \text{(Eq. 3)}$$

The formula for the standard error of the difference between the means is substituted in the formula for t, giving:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{s_p^2}\sqrt{\frac{1}{N_1} + \frac{1}{N_2}}} \qquad \text{(Eq. 4)}$$

where:

$\bar{x}_1$ = the average of test method no. 1

$\bar{x}_2$ = the average of test method no. 2

N_1 = no. of measurements by test method no. 1

N_2 = no. of measurements by test method no. 2

To compare the averages of three or more sets of measurements (the t test can compare only two sets), an extension of the analysis of variance[3], the statistic w, is used. If the absolute differences between the averages of all the sets of data are less than w, then it is considered that no differences exist among the averages. The critical value of w is computed thus:

$$w = q_{.95} S_c / \sqrt{n} \qquad \text{(Eq. 5)}$$

where:

w = computed critical value from standardized range

$q_{.95}(t,v)$ = a statistic that is a function of the number of data sets, t, and degrees of freedom, v

S_c = pooled standard deviation

n = number of data sets

SECTION 4
SURVEY MATERIALS

SULFUR DIOXIDE SAMPLES

The sample material was composed of freeze-dried mixtures of sodium sulfite and potassium tetrachloromercurate (TCM) contained in 5-ml glass ampoules. Sample sets consisted of five ampoules containing 4 to 64 μg of SO_2 equivalent per container. The sample material was stored at -20°C in the QAD Repository to sustain the integrity of the SO_2 activity, which was confirmed by periodic retesting. Analyses were performed by the reference method for the determination of SO_2 in the atmosphere (pararosaniline method).[5] The sample forms a dichlorosulfitomercurate complex when solubilized in 0.04N TCM. This complex is reacted with pararosaniline and formaldehyde to form intensely colored pararosaniline sulfonic acid. The absorbance of the solution is measured spectrophometrically at 548 nm.

At least 15 samples from each concentration level were analyzed (Table 1) and the analyzed values are the reference (expected) values of surveys 0479 and 1079 (surveys are numbered by month and year). In addition, independent corroborative tests were conducted by another laboratory. The presumption was that each sample was collected in 50 ml of absorbing reagent with a total sample air volume of 30Ø.

NITROGEN DIOXIDE SAMPLES

The samples consisted of 5 mL of aqueous sodium nitrite contained in glass ampoules. A set consisted of 5 ampoules. When mixed with caustic absorbing reagent, the samples simulated ambient samples ranging in concentration from 0.17 to 1.00 μg/mL.

Analysis of 15 samples in each concentration level was performed using an equivalent method for the determination of NO_2 in ambient air.[6] Measurements were made spectrophotometrically at 540 nm. The values contained in Table 2 were the reference (expected) values for surveys 0679 and 1279. Values are based on the entire sample being diluted to 50 mL with absorbing reagent.

TABLE 1. CONCENTRATIONS OF SO_2 SURVEY SAMPLES

Survey 0479					Survey 1079				
	μg SO_2		μg SO_2/m3			μg SO_2		μg SO_2/m3	
Sample No.	$\bar{x}$*	s	$\bar{x}$*	s	Sample No.	$\bar{x}$†	s	$\bar{x}$†	s
1	4.18	0.69	13.9	2.3	1	4.04	0.30	13.5	1.0
3	28.0	0.42	93.3	1.4	2	11.6	0.25	38.5	0.83
4	44.5	0.37	148	1.2	3	24.0	0.92	80.0	3.1
5	63.5	0.42	212	1.4	4	37.5	1.30	125	4.3
					5	49.4	0.87	165	2.9

*n = 15
†n = 25

TABLE 2. CONCENTRATIONS OF NITROGEN DIOXIDE SURVEY SAMPLES

Survey 0679			Survey 1279		
	μg/mL NO_2			μg/mL NO_2	
Sample No.	$\bar{x}$*	s	Sample No.	$\bar{x}$*	s
1	0.259	0.0018	1	0.172	0.0065
2	0.405	0.0034	2	0.342	0.0046
3	0.514	0.0019	3	0.595	0.0076
4	0.700	0.0018	4	0.746	0.0174
5	0.935	0.0032	5	1.00	0.0275

*n = 15

CARBON MONOXIDE SAMPLES

Samples consisted of compressed gas mixtures of carbon monoxide (CO) and artificial air. Also contained in each sample was 2 ppm of methane (CH_4) and approximately 365 ppm of carbon dioxide (CO_2). Aluminum cylinders were used in the surveys. Sample concentrations ranged from 3 to 44 ppm of CO. Each participant received a set of three cylinders, one from each of three concentration levels.

Verification testing was accomplished by use of a non-dispersive infrared analyzer (NDIR). Fifteen samples from each concentration level were analyzed by QAD and an independent testing laboratory. Table 3 lists the reference (expected) values for surveys 0379 and 0979.

SULFATE-NITRATE SAMPLES

Samples consisted of 1.9 x 20 cm (0.75 x 8 in.) glass fiber filter strips with depositions of potassium sulfate (K_2SO_4) and lead nitrate ($Pb[NO_3]_2$). Filter strip samples included concentrations of various SO_4 and NO_3 concentrations. Each strip was sealed in a plastic envelope. The concentrations of sulfate ranged from approximately 1.5 to 29 $\mu g/m^3$. Nitrate levels spanned between 1.5 and 12 $\mu g/m^3$. Concentrations were determined using the requisite filter dimensions of 20 x 25.4 cm (8 x 10 in) and a collected air volume of 2000 m^3. Presuming that gravimetric preparation and transfer onto the filter strips could be carried out more accurately than could existing analytical methods, the reference (expected) values were obtained theoretically from the deduced mass of inorganic salts deposited on the filters. Verification analyses assured that the accuracy and precision of the samples were within prescribed limits. The sulfate concentrations have been given in Table 4 and the nitrate values are listed in Table 5. These were the values which were applied to surveys 0279 and 0879.

LEAD SAMPLES

Samples were composed of 1.9 x 20 cm (0.75 by 8 in) glass fiber filter strips with depositions of lead nitrate ($Pb[NO_3]_2$). Filter strip sample sets contained combinations of various lead concentrations, each sealed in a plastic envelope. The lead content ranged from 1.5 to 12.9 $\mu g/m^3$. Concentrations were calculated presuming that the samples were collected on the prescribed 20 x 25.4 cm (8 x 10 in) hi-vol filter with a total air volume of 2000 m^3.

The precision and accuracy measurements of this sample material were done by atomic absorption analysis. Table 6 lists the reference (expected) values used in surveys 1079 and 0779.

TABLE 3. CONCENTRATIONS OF CARBON MONOXIDE SURVEY SAMPLES

Survey 0379			Survey 0979		
	ppm CO			ppm CO	
Sample No.	x*	s	Sample No.	x*	s
1	6.53	0.06	1	2.98	0.02
2	19.8	0.19	2	14.8	0.06
3	43.7	0.26	3	33.8	0.12

*n = 15

TABLE 4. CONCENTRATIONS OF SULFATE SURVEY SAMPLES

Survey 0279			Survey 0879		
Sample No.	μg $SO_4^=$/strip	μg $SO_4^=/m^3$/filter	Sample No.	μg $SO_4^=$/strip	μg $SO_4^=/m^3$/filter
2	250.0	1.5	5	1200.0	7.2
6	1000.0	6.0	0	1516.7	9.1
0	1750.0	10.5	4	2183.3	13.1
3	2500.0	15.0	3	3950.0	23.7
1	3250.0	19.5	2	4800.0	28.8
4	4000.0	24.0			

TABLE 5. CONCENTRATIONS OF NITRATE SURVEY SAMPLES

Survey 0279			Survey 0879		
Sample No.	μg NO_3^-/strip	μg NO_3^-/m^3/filter	Sample No.	μg NO_3^-/strip	μg NO_3^-/m^3/filter
0	250.0	1.5	5	200.0	1.2
1	600.0	3.6	0	566.7	3.4
2	950.0	5.7	2	1000.0	6.0
4	1300.0	7.8	4	1383.3	8.3
5	1650.0	9.9	3	1700.0	10.2
3	2000.0	12.0			

TABLE 6. CONCENTRATIONS OF LEAD SURVEY SAMPLES

Survey 0179					Survey 0779				
Sample No.	µg Pb/test strip		µg/m^3/filter		Sample No.	µg Pb/test strip		µg/m^3/filter	
	$\bar{x}$*	s	$\bar{x}$*	s		$\bar{x}$*	s	$\bar{x}$*	s
3	243.4	6.09	1.46	0.037	0	587.9	13.52	3.53	0.081
4	586.7	14.89	3.52	0.089	1	2143.1	33.30	12.86	0.200
5	899.0	30.07	5.39	0.180	2	974.7	24.08	5.85	0.144
6	1908.2	70.11	11.45	0.421	3	1731.4	27.58	10.39	0.165
7	1246.2	36.83	7.48	0.221	4	1320.7	18.93	7.92	0.114
8	1584.6	62.17	9.51	0.373	5	196.8	3.45	1.18	0.021

*$n = 10$

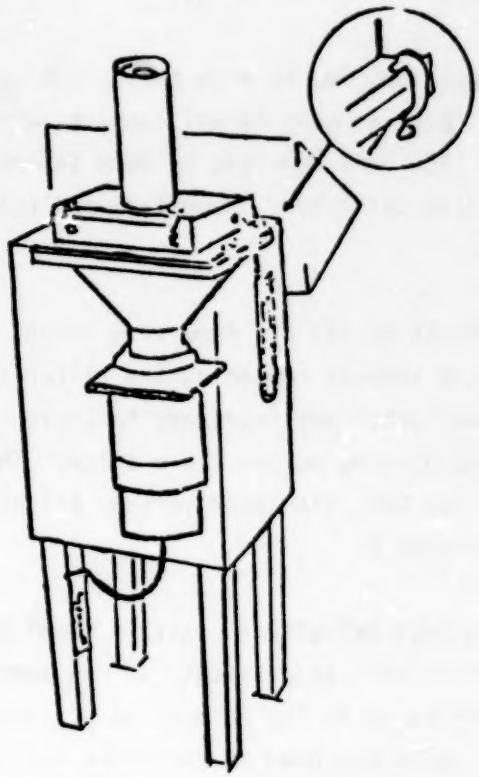


Figure 1. Reference flow device mounted on high volume sampler.

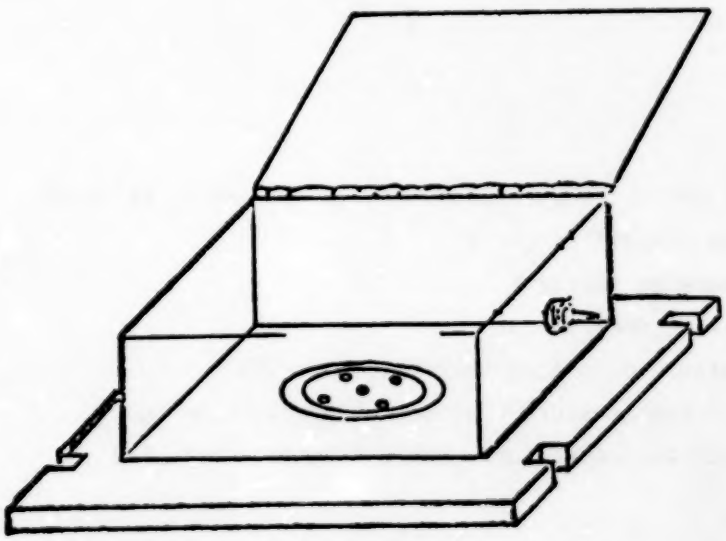


Figure 2. Reference flow device with resistance plate.

HIGH VOLUME REFERENCE FLOW DEVICE (ReF)

A single ReF was supplied to each participating agency. Organizations were instructed to check as many hi-vol sampling units as feasible within the allotted time. The unit received by each laboratory consisted of a modified orifice, wind deflector, manometer, and resistance plates (to change flow rates).

During measurement of the air flow of a hi-vol sampler, the ReF was mounted on top of the sampler replacing the filter face plate as shown in Figure 1. A wind deflector was necessary to prevent fluctuation in the readings due to wind blowing across the orifice. The resistance plates, when inserted into the ReF, simulated various filter loading conditions as illustrated in Figure 2.

By calibrating each ReF with a positive displacement meter (roots meter), in conjunction with measurements of pressure drops and temperatures, a calibration curve in the form of an orifice equation was derived. The equation shown below was used to determine the "K" orifice constant for each unit.

$$Q_1 = AYC \sqrt{\frac{\Delta P \; T_1}{P_1}} \qquad \text{(Eq. 6)}$$

where:

Q_1 = volumetric flow at conditions of T_1 and P_1 (m^3/min)
A = area of orifice (in^2)
Y = expansion factor
C = orifice coefficient
ΔP = pressure drop across orifice (in H_2O)
P_1 = upstream pressure (barometric pressure, mm Hg)
T_1 = upstream temperature (ambient temperature, °K)

Because A is constant for a given orifice, and Y and C are essentially constant over the flow range in question, a new orifice constant "K" was defined as:

$$K = AYC \qquad \text{(Eq. 7)}$$

Thus, the orifice equation becomes:

$$Q_1 = K \sqrt{\frac{\Delta P \; T_1}{P_1}} \qquad \text{(Eq. 8)}$$

During calibration of the ReF, Q_1, ΔP, T_1 and P_1 were also measured. The constant K was determined by regressing a series of Q_1 measurements onto the square root of the values under the radical.

During the survey, operating personnel measured ΔP, T_1 and P_1. By knowing K, the "true flow" can be calculated. This flow was compared with the flow measured by the high volume sensor to determine the accuracy of flow measurements.

SECTION 5
RESULTS

SULFUR DIOXIDE

Test Methods

Approximately 80 percent of the respondents in 0479 and 1079 surveys used the manual, and 20 percent the automated pararosaniline procedures. The few remaining laboratories used other methods. The results of the two principle methods were subjected to the t test at the 95 percent confidence level. The difference between the averages was not statistically significant. The F test showed that the two methods do not differ with regard to variability.

Agency Apportionment

Participation in the April 1979 SO_2 survey decreased by 12 percent from the previous year[7], with the October 1979 survey continuing at about the same as 1978. The reduction was largely accounted for by decreased use of the pararosaniline method by state agencies. The number of users of the pararosaniline method stabilized at around 100. The distribution of agencies in the surveys is shown in Table 7.

TABLE 7. AGENCY APPORTIONMENT OF SULFUR DIOXIDE SURVEYS

Agency	Survey 0479, %	Survey 1079, %
Regional (Federal)	1.8	0.0
State Agencies	37.8	39.0
Local Agencies	42.4	43.8
Industrial/Contractor	18.0	16.2
Foreign	0.0	1.0

Data Summary

Survey results are summarized in Table 8, with all methods included. Results according to analytical method are given in Table 9. Table 10 gives the frequency distribution of the results in terms of percent of expected values. The values termed expected values are the best estimates of the true concentrations and are derived from the analyses performed by EPA laboratories, a commercial corroborative laboratory, and the manufacturer's analyses. The sample material was evaluated as to stability, homogeneity, and accuracy before use in the survey.

Anomalous measurements are excluded from the summary tables. In survey 0479, 7 percent, and in survey 1079, 4.6 percent of the measurements were excluded by Chauvenet's Criterion.

TABLE 8. SUMMARY OF SULFUR DIOXIDE PROFICIENCY SURVEYS

Sample no.	Respondents*	Expected value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0479 (April 1979)					
1	100	13.9	14.15	4.85	2.17 - 25.76
3	105	93.3	92.56	7.97	70.74 - 109.10
4	103	148.3	154.30	10.45	126.51 - 175.68
5	105	212.7	214.48	15.03	170.80 - 256.99
Survey 1079 (October 1979)					
1	101	13.5	12.63	5.00	1.08 - 33.30
2	103	38.5	35.80	6.57	10.13 - 54.10
3	102	80.0	77.26	8.14	48.14 - 108.40
4	103	125	125.24	11.31	88.00 - 166.50
5	104	165	165.62	14.16	104.22 - 206.97

*With outliers removed.

TABLE 9. SULFUR DIOXIDE BY ANALYTICAL METHOD

($\mu g/m^3$)

Survey 0479* (April 1979)

Sample No.	Pararosaniline - manual			Pararosaniline - automated		
	N†	Mean	Std. dev.	N	Mean	Std. dev.
1	78	14.87	7.19	22	14.33	5.06
3	83	92.19	10.06	22	91.34	8.34
4	81	153.59	13.95	22	153.73	12.98
5	84	214.30	16.37	21	210.08	17.68

Survey 1079* (October 1979)

Sample no.	Pararosaniline-manual			Pararosaniline-automated			All others		
	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
1	79	13.09	9.12	20	11.75	4.44	2	15.13	0.10
2	81	35.25	9.70	20	35.32	9.28	2	36.08	1.68
3	80	76.22	13.85	20	75.26	11.90	2	71.20	0.99
4	81	123.27	16.86	20	121.26	20.38	2	127.28	13.04
5	82	166.12	27.00	20	169.14	24.49	2	168.94	9.70

*Outliers removed.
†Number of respondents.

TABLE 10. SULFUR DIOXIDE, PERCENT OF MEASUREMENTS WITHIN INDICATED PERCENT OF EXPECTED VALUES

Survey 0479					Survey 1079				
Sample no.	10%	20%	30%	50%	Sample no.	10%	20%	30%	50%
1	20	35	57	82	1	34	57	66	79
3	74	97	99	100	2	54	80	85	94
4	72	100	100	100	3	72	89	92	95
5	79	100	100	100	4	81	92	96	98
					5	78	93	96	97

The mean values from survey 0479, plotted against the expected values, gave a linear relationship, as follows:

$$y = a + bx \qquad \text{(Eq. 7)}$$

where:

y = survey average
x = expected value
a = y intercept = -0.0957
b = slope = 1.0164
R^2 = coefficient of linearity squared = 0.9991

y = -0.0957 + 1.0164 (expected value)

The plot of the survey means (y) against the expected value (x) has been shown in Figure 3.

The means for survey 1079, plotted against the expected values, gave a linear relationship, as follows:

Survey average = -2.5100 + 1.0168 (expected value)

R^2 = 0.9996

The plot of the survey means (y) against the expected values (x) is shown in Figure 4.

Summary

Proficiency surveys for SO_2 were conducted in April and October 1979. Approximately 100 participants completed each of the surveys. The pararosaniline method predominated with 80 percent of the laboratories using that procedure. No systematic discrepancies or substantial bias were found in the SO_2 surveys.

NITROGEN DIOXIDE

Test Methods

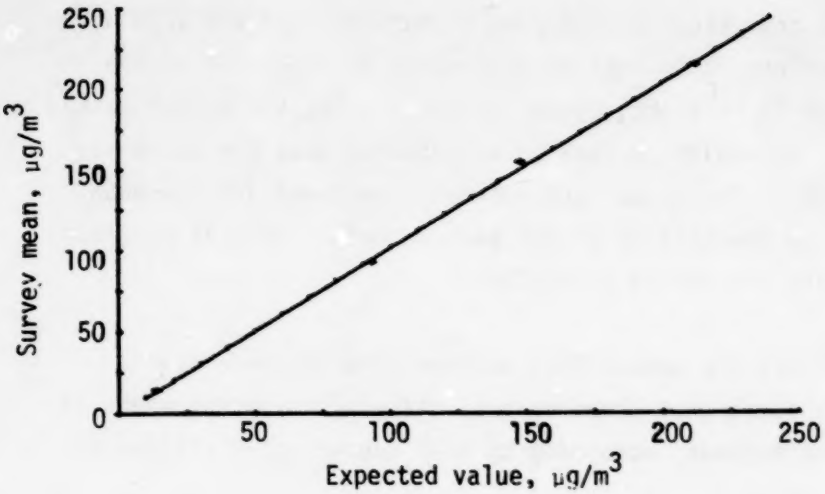
The predominant analytical method used in surveys 0679 and 1279 was the manual sodium arsenite colorimetric procedure; 72.7 percent of the 0679 respondents used it. Slightly fewer reported using the manual method in the 1279 survey. Around 21 percent of respondents used the automated sodium arsenite method. The manual and automated Saltzman and TGS-ANSA manual methods made up the balance of the test methods. Several participants did not indicate the method of analysis.

The averages of all the manual test methods were compared by the statistic w. It was found that there were no differences in the means of the several different methods, according to this conservative statistical test.

The variability between the two dominant methods was tested by the F test. In the 0679 survey, the variability of samples 4 and 5 was greater by the manual arsenite method, while in the 1279 survey, samples in the same concentration range exhibited greater variability by the automated method. There was no reason to suspect that there was any inherent difference in variability between the two test methods.

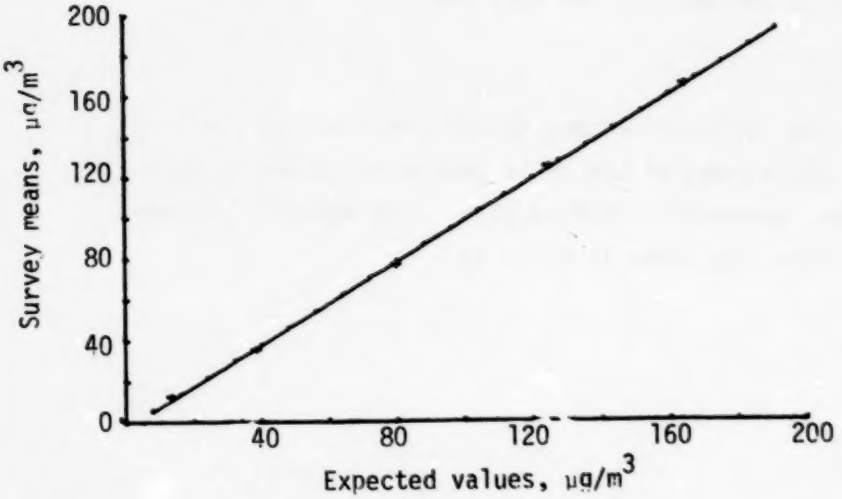
Agency Apportionment

Participation in the 1979 Proficiency Survey continued at close to the 1978 level[7], with the second of the twice yearly tests having approximately 11 percent fewer laboratories taking part. The agencies included in the NO_2 surveys by type are shown in Table 11.



x	y
13.9	14.15
93.3	92.56
148.3	154.3
212.7	214.5

Figure 3. Means of SO_2 survey 0479 vs. expected values.



x	y
13.5	12.63
38.5	35.80
80.0	77.26
125.0	125.2
165.0	165.6

Figure 4. Mean values of SO_2 survey 1079 vs. expected values.

TABLE 11. AGENCY APPORTIONMENT OF NITROGEN DIOXIDE SURVEYS

Agency	Survey 0679, %	Survey 1279, %
Regional (Federal)	1.1	0.0
State Agencies	42.5	33.3
Local Agencies	44.7	52.6
Industrial/Contractor	10.6	12.8
Foreign	1.1	1.3

Data Summary

Survey results are tabulated in Table 12 with all methods included. Table 13 lists the results by specific analytical method. Frequency distributions by percent of the expected value are shown in Table 14. Table 14 shows the percents of reported measurements which lie within the indicated percent (10, 20, 30, or 50) of the expected value. The expected values, or best estimates of the true concentrations, were derived from analyses performed by the QAD, by a commercial testing laboratory and by the manufacturer. The sample material was tested for conformity to established criteria for precision and accuracy.

TABLE 12. SUMMARY OF NITROGEN DIOXIDE PROFICIENCY SURVEYS

Sample No.	Respondents*	Expected value µg/mL	Survey mean µg/mL	Survey std. dev. µg/mL	Survey interval µg/mL
Survey 0679 (June 1979)					
1	88	0.259	0.26	0.02	0.21 - 0.30
2	88	0.405	0.40	0.02	0.34 - 0.45
3	88	0.514	0.51	0.03	0.39 - 0.62
4	87	0.700	0.71	0.03	0.62 - 0.78
5	86	0.935	0.95	0.04	0.83 - 1.07
Survey 1279 (December 1979)					
1	76	0.172	0.18	0.04	0.09 - 0.44
2	78	0.342	0.35	0.05	0.14 - 0.55
3	76	0.595	0.59	0.07	0.22 - 0.73
4	77	0.746	0.74	0.09	0.28 - 0.90
5	76	1.000	0.97	0.12	0.34 - 1.16

*With outliers removed.

TABLE 13. NITROGEN DIOXIDE BY ANALYTICAL METHOD
µg/mL

Survey 0679* (June 1979)	Saltzman-manual			Sodium arsenite-manual			Sodium arsenite-automated			TGS-ANSA manual			All others		
Sample No.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
1	3	0.26	0.01	64	0.26	0.02	18	0.26	0.02	1	0.26	0.00	2	0.26	0.01
2	3	0.42	0.02	64	0.40	0.03	18	0.40	0.02	1	0.40	0.00	2	0.39	0.00
3	3	0.52	0.01	64	0.52	0.04	18	0.50	0.06	1	0.51	0.00	2	0.70	0.26
4	3	0.72	0.01	64	0.71	0.05	18	0.70	0.02	1	0.69	0.00	1	0.73	0.00
5	3	0.97	0.04	62	0.95	0.07	18	0.94	0.02	1	0.95	0.00	2	0.99	0.01

Survey 1279* (December 1979)	Saltzman-manual			Saltzman-automated			Sodium arsenite-manual			Sodium arsenite-automated			TGS-ANSA-manual			All others		
Sample No.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
1	3	0.17	0.02	1	0.17	0.00	48	0.18	0.02	16	0.19	0.02	2	0.20	0.02	1	0.18	0.00
2	3	0.36	0.01	1	0.32	0.00	51	0.36	0.03	16	0.36	0.02	2	0.34	0.04	1	0.38	0.00
3	3	0.59	0.05	1	0.59	0.00	49	0.61	0.03	16	0.62	0.04	2	0.58	0.06	1	0.62	0.00
4	3	0.71	0.09	1	0.71	0.00	50	0.75	0.04	16	0.74	0.09	2	0.73	0.02	1	0.76	0.00
5	2	1.02	0.02	1	0.96	0.00	50	0.99	0.05	16	1.01	0.07	2	0.99	0.05	1	1.00	0.00

*With outliers removed.

TABLE 14. PERCENT OF NITROGEN DIOXIDE MEASUREMENTS WITHIN INDICATED PERCENT OF EXPECTED VALUES

Survey 0679					Survey 1279				
Sample no.	10%	20%	30%	50%	Sample no.	10%	20%	30%	50%
1	86	97	100	100	1	63	86	92	93
2	90	99	100	100	2	81	91	94	94
3	85	92	97	99	3	88	92	95	95
4	93	97	99	100	4	86	95	95	95
5	90	97	100	100	5	89	93	95	95

The means from survey 0679, plotted against the expected values, gave a linear relationship, as follows:

Survey average = -0.0121 + 1.0276 (expected value)
R^2 = 0.9997

The plot of the survey means (y) against the expected values (x) is shown in Figure 5.

The means from survey 1279, plotted against the expected values, gave a linear relationship, as follows:

Survey average = 0.0205 + 0.9553 (expected value)
R^2 = 0.9997

The plot of the survey means (y) against the expected values (x) has been shown in Figure 6.

Summary

Proficiency Surveys in 1979 for NO_2 were conducted in June with approximately 90 participants and in December with close to 80. The analytical method used by approximately 70 percent of the respondents was the manual sodium arsenite procedure. No systematic discrepancies or substantial bias were apparent in the NO_2 survey data.

CARBON MONOXIDE

Test Methods

Of the test methods listed on the survey information forms, the NDIR method dominated, with 91 percent of the laboratories using that method in the 0379 survey and 87 percent in the 0979 test. Facilities using the GC method increased from 6 to 12 percent during the biannual testing period. Other methods were reported being used by approximately 2 percent of the respondents.

Results by the two principal methods were compared by the t test to determine whether differences in the averages were significant. In survey 0379 they were not; in 0979 survey, the difference was significant for sample number 2. Although the difference in the averages of only one of six samples was statistically significant, the GC survey standard deviations were substantially larger in five of six samples.

The great disparity in of the number of laboratories using the two methods was a factor in comparing the results. Were the number of users of the GC method equivalent with those using the NDIR method, it would be expected that the GC standard deviation would be larger yet. The 1979 and previous survey results lead to the conclusion that the precision of the GC method is less than that of the NDIR method. The F test supported the same conclusion. Evaluating the ratio of the variances of the two methods

made clear that the variablity of the GC method exceeds that of the NDIR procedure.

Agency Apportionment

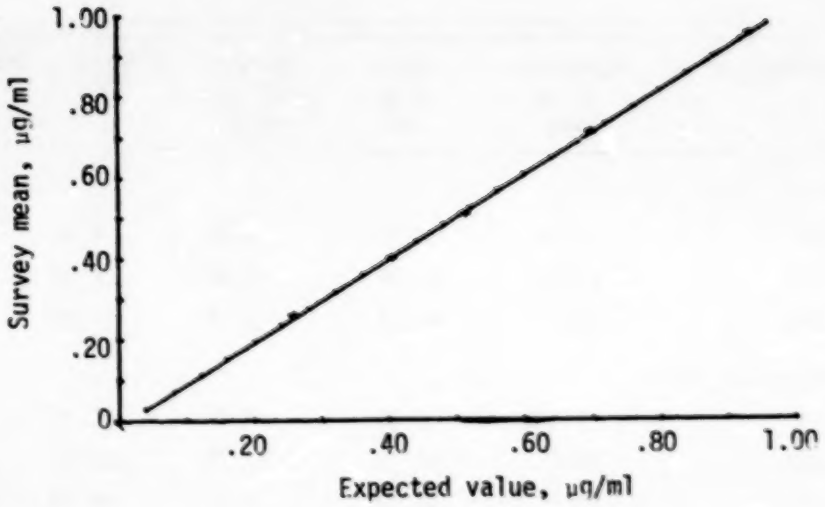
Laboratories taking part in the 1979 CO Proficiency Surveys numbered close to those participating during the previous year[7]. State laboratory response increased by approximately 8 percent, while local agencies were about 9 percent less. The agencies comprised in the CO surveys are shown in Table 15.

Data Summary

The results of the 1979 CO surveys, with all methods included, are summarized in Table 16. The results arranged by analytical test method, are shown in Table 17. Table 18 consists of the percentiles of reported measurements which lie within the indicated percent (10, 20, 30 and 50) of the expected value. The concentrations identified as expected values were confirmed as the "true values" by analyses of the QAD corroborative tests, and the analysis of the manufacturer.

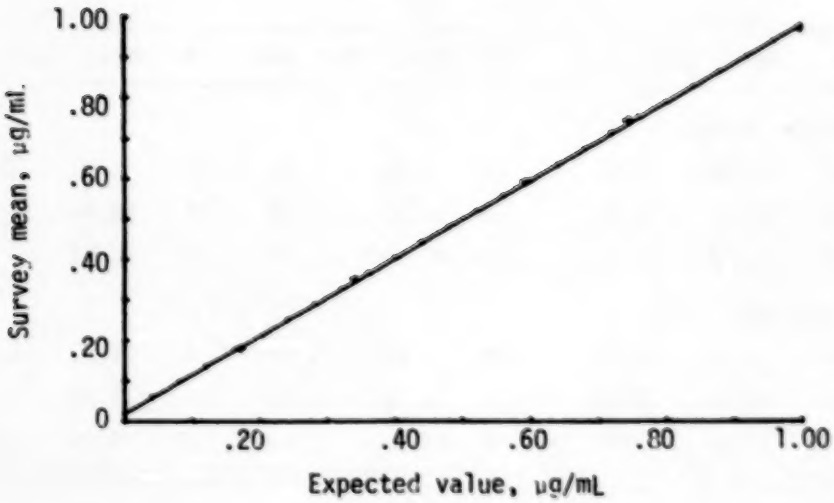
TABLE 15. AGENCY APPORTIONMENT OF CARBON MONOXIDE SURVEYS

Agency	Survey 0379, %	Survey 0979, %
ERC (Federal)	0.3	0.9
Regional (Federal)	2.0	1.3
State Agencies	46.9	48.9
Local Agencies	46.2	41.7
Industrial/Contractor	2.3	4.1
Foreign	2.3	3.1



x	y
0.259	0.26
0.405	0.40
0.514	0.51
0.700	0.71
0.935	0.95

Figure 5. Mean values of NO_2 survey 0679 vs. expected values.



x	y
0.172	0.18
0.342	0.35
0.595	0.59
0.746	0.74
1.000	0.97

Figure 6. Mean values of NO_2 survey 1279 vs. expected values.

TABLE 16. SUMMARY OF CARBON MONOXIDE PROFICIENCY SURVEYS

Sample No.	Respondents*	Expected value ppm	Survey mean ppm	Survey std. dev. ppm	Survey interval ppm
Survey 0379 (March 1979)					
1	291	6.53	6.39	0.53	4.92 - 8.50
2	295	19.8	20.08	0.89	17.30 - 23.00
3	294	43.7	44.14	1.51	38.23 - 49.70
Survey 0979 (September 1979)					
1	290	2.98	2.73	0.48	1.25 - 4.75
2	268	14.8	14.75	0.75	12.24 - 17.30
3	297	33.8	34.14	1.37	29.50 - 39.00

*With outliers removed.

TABLE 17. CARBON MONOXIDE BY ANALYTICAL METHOD
(ppm)

	NDIR			GC			All other		
Sample No.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
Survey 0379* (March 1979)									
1	265	6.36	0.66	16	6.16	1.05	10	6.13	0.67
2	268	20.03	1.01	16	19.78	1.42	11	19.94	0.62
3	270	44.12	1.41	13	44.16	2.90	11	42.07	7.42
Survey 0979* (September 1979)									
1	255	2.75	0.61	31	2.69	0.48	4	4.73	3.52
2	229	14.77	0.82	35	14.36	1.06	4	14.84	1.01
3	259	34.07	1.48	35	34.31	2.03	3	32.28	3.97

*Outliers removed.

TABLE 18. PERCENT OF CARBON MONOXIDE MEASUREMENTS WITHIN INDICATED PERCENT OF EXPECTED VALUE

Survey 0379					Survey 0979				
Sample No.	10%	20%	30%	50%	Sample No.	10%	20%	30%	50%
1	81	94	98	100	1	46	77	91	97
2	93	99+	100	100	2	92	100	100	100
3	99	100	100	100	3	97	100	100	100

The mean values from survey 0379, plotted against the expected values, gave a linear relationship, as follows:

Survey average = -0.1461 + 1.0145 (expected value)
R^2 = 1.0000

The plot of the survey means (y) against the expected values (x) has been shown in Figure 7.

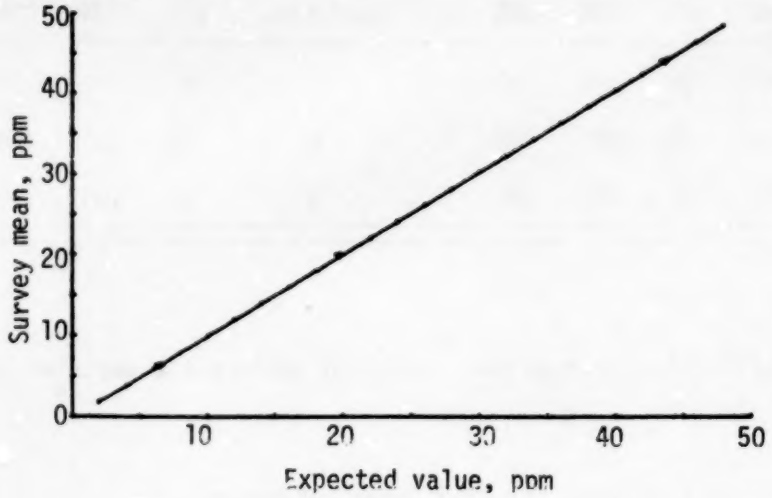
The means from survey 0979, plotted against the expected values, gave a linear relationship, as follows:

Survey average = -0.3078 + 1.0179 (expected value)
R^2 = 1.0000

A plot of the survey mean (y) against the expected values (x) is shown in Figure 8.

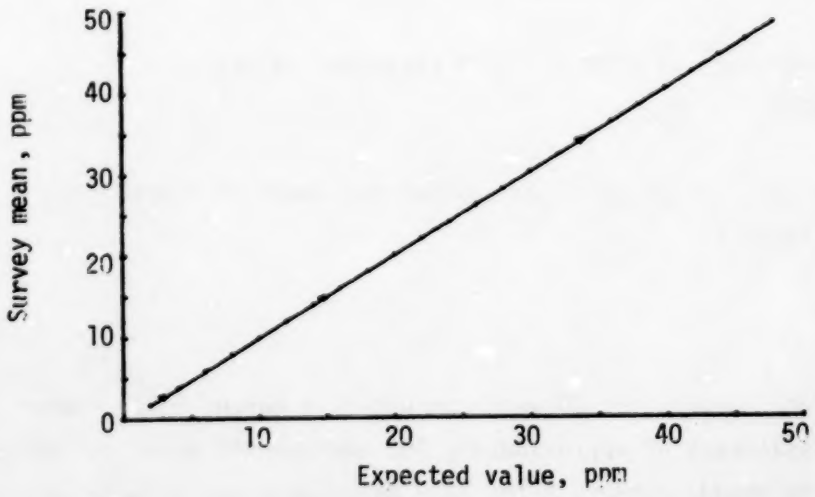
Summary

Proficiency Surveys for CO were conducted in March and September 1979. Operational assessment of approximately 300 instruments were included in each of the semiannual surveys. The NDIR method was employed by approximately



x	y
6.53	6.39
19.8	20.08
43.7	44.14

Figure 7. Mean values of CO survey 0379 vs. expected values.



x	y
2.98	2.73
14.8	14.75
33.8	34.10

Figure 8. Mean values of CO survey 0979 vs. expected values.

90 percent of the survey respondents. No systematic discrepancies or substantial bias were identified in the CO surveys. The precision of the NDIR method proved to be generally superior to that of the GC procedure.

SULFATE

Test Method

Participants in the 0279 and 0879 surveys employed four principal test methods. They were the automated methylthymol blue, manual barium chloride, manual Sulfa-Ver© and ion chromatograph procedures. There was little change in the relative use of the methods between the semiannual tests, with approximately 38 percent using the methylthymol blue, 30 percent the manual barium chloride, and 16 percent the Sulfa-Ver© methods. Ten percent used the sensitive and accurate ion chromatographic method. The remainder utilized other methods or the methodology was undetermined.

The averages of all the named test methods were compared by an extension of the analysis of variance at the 5 percent significance level. Since the absolute differences between the means of the separate methods were less than the critical value of w, there was no reason to believe that the averages differed. The manual and automated barium chloride methods were the most variable.

Agency Apportionment

Agency balance in the 1979 surveys differed little from the distribution during the previous survey period[7]. State and local agencies accounted for better than 70 percent of the participation. The classification of agencies involved in the 1979 surveys is shown in Table 19.

TABLE 19. AGENCY APPORTIONMENT OF SULFATE SURVEYS

Agency	Survey 0279, %	Survey 0879, %
ERC (Federal)	1.5	1.7
Regional (Federal)	1.5	1.7
State Agencies	44.0	41.6
Local Agencies	27.3	26.7
Industrial/Contractor	22.7	21.6
Foreign	3.0	6.7

Data Summary

The survey results of all methods are tabulated in Table 20. Results listed by analytical method are shown in Table 21. Frequency distributions of the percent of measurements falling within the indicated percent of the expected value are presented in Table 22. The expected values used in the sulfate surveys were the theoretical concentration of sulfate ion of an inorganic salt which was deposited on glass fiber filter strips. The theoretical values were confirmed by a corroborative laboratory and by the QAD.

Anomalous measurements are excluded from the summary tables. Approximately 3 percent of the reported measurements in both surveys were rejected on the basis of Chauvenet's Criterion and the reviewers' judgment.

TABLE 20. SUMMARY OF SULFATE PROFICIENCY SURVEYS

Sample no.	Respondents	Expected value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0279 (February 1979)					
0	65	10.50	10.61	2.21	6.65 - 21.60
1	65	19.50	18.96	1.73	14.10 - 23.64
2	65	1.50	1.96	1.17	0.30 - 5.60
3	65	15.00	14.74	1.34	11.70 - 18.03
4	65	24.00	23.80	2.22	16.48 - 31.80
5	65	6.00	5.75	1.13	3.06 - 9.15
Survey 0879 (August 1979)					
0	59	9.10	8.38	1.25	3.00 - 11.11
2	58	28.80	27.42	2.57	20.00 - 33.60
3	60	23.70	22.90	2.58	14.00 - 30.11
4	58	13.10	12.16	1.58	6.45 - 15.90
5	59	7.20	6.77	1.18	3.50 - 10.13

*With outliers removed.

TABLE 21. SULFATE BY ANALYTICAL METHOD
($\mu g/m^3$)

Survey 0279* (February 1979)	Methylthymol blue-automated			Barium chloride-manual			Barium chloride-automated			Sulfa-Ver-manual			Ion chromatograph		
Sample No.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
0	26	10.32	1.00	20	13.05	6.71	3	9.78	2.74	10	10.14	1.08	6	9.47	1.30
1	26	18.42	1.95	20	19.20	3.23	3	21.78	1.97	10	18.50	2.11	6	19.13	1.12
2	26	1.60	0.87	20	2.72	2.07	3	0.93	0.90	10	1.99	1.07	6	1.59	0.60
3	26	14.60	1.07	20	16.12	3.74	3	15.14	2.62	10	14.04	0.72	6	12.73	4.01
4	26	23.22	1.20	20	25.87	5.85	3	28.07	7.85	10	23.71	2.03	6	23.41	1.23
5	26	5.85	0.74	20	6.69	2.64	3	5.10	1.97	10	5.27	0.78	6	5.71	0.95

Survey 0879* (August 1979)	Methylthymol blue-manual			Methylthymol blue-automated			Barium chloride-manual			Barium chloride-automated			Sulfa-Ver-manual			Ion chromatograph		
Sample No.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
0	1	6.80	0.00	22	8.41	0.82	18	8.48	1.96	1	7.30	1.96	10	8.44	3.16	7	9.31	2.36
2	1	25.20	0.00	21	27.12	2.56	18	27.78	3.14	1	23.35	0.00	10	28.61	3.90	7	27.65	1.20
3	1	21.00	0.00	22	22.15	4.06	19	23.02	3.11	1	20.70	0.00	10	24.12	2.93	7	22.06	1.59
4	1	10.10	0.00	22	12.27	1.11	17	12.17	3.20	1	11.07	0.00	10	13.85	4.67	7	12.05	0.71
5	1	4.70	0.00	22	6.80	0.75	18	6.74	1.55	1	5.46	0.00	10	7.00	1.36	7	6.88	0.88

*Outliers removed.

TABLE 22. PERCENT OF SULFATE MEASUREMENTS WITHIN INDICATED PERCENT OF EXPECTED VALUE

Survey 0279					Survey 0879				
Sample No.	10%	20%	30%	50%	Sample No.	10%	20%	30%	50%
0	63	80	89	94	0	56	83	88	93
1	75	89	95	100	2	76	91	98	100
2	25	40	43	57	3	67	92	98	100
3	74	91	97	97	4	59	84	93	95
4	75	92	94	97	5	54	80	88	98
5	52	74	82	95					

The means from survey 0279, plotted against the expected values, gave a linear relationship, as follows:

Survey average = 0.2542 + 0.9712 (expected value)

A plot of the survey 0279 means (y) against the expected values (x) is shown in Figure 9.

The mean values from survey 0879, plotted against the expected values, gave a linear relationship, as follows:

Survey average = -0.3604 + 0.09699 (expected value)
R^2 = 1.0000

A plot of the survey means (y) against the expected values (x) is shown in Figure 10.

Summary

Proficiency Surveys for $SO_4^=$ were conducted in February and August 1979. Approximately 60 laboratories participated. Better than 70 percent of the roster of participating laboratories comprised state and local agencies. Six test methods were employed; the methylthymol blue and the manual barium chloride procedures dominated. Other major methods used were the Sulfa-Ver® and ion chromatography. No systematic discrepancies occurred. The barium chloride procedures exhibited the greatest variability of the test methods.

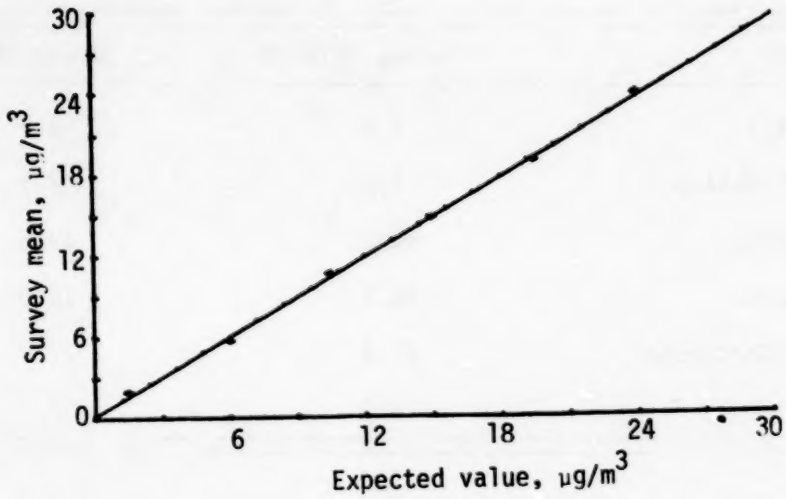
NITRATE

Test Method

Over half of the respondents reported using the automated cadmium reduction method; the balance used one of eight other methods. Choice of analytical method did not change notably between the biannual tests, though participation was reduced in the later survey. The dominant unlisted method was the ion chromatographic procedure. Others were phenoldisulfonic acid, brucine, specific ion electrode, Szechrome® and ultraviolet spectrophotometric procedures. The averages of all the methods, including all the unlisted methods, were compared by an extension of the analysis of variance at the 5 percent significance level. Since the absolute differences between the averages were less than the critical value of w, it was concluded that the averages did not differ. No single method was conspicuously imprecise.

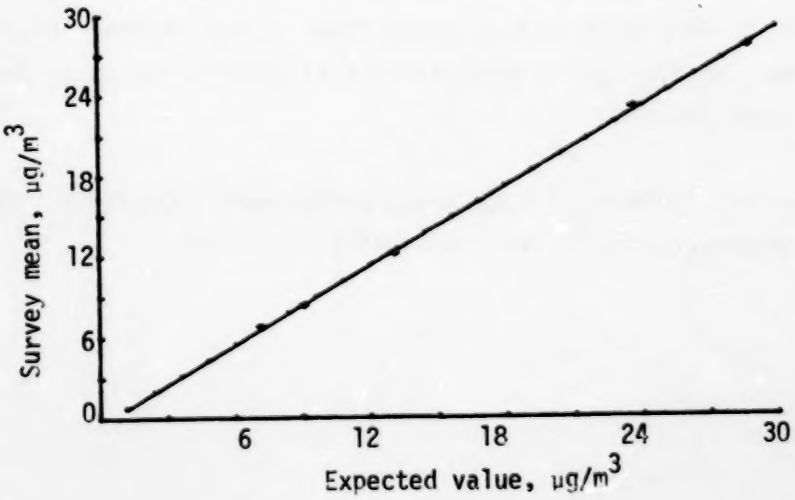
Agency Apportionment

Involvement of state agencies in the nitrate surveys decreased by approximately 3 percent from the previous survey year[7] with a corresponding increase in local air monitoring boards. State and local offices embodied 65 percent of the total participation. The divisional composition of the surveys is shown in Table 23.



x	y
10.50	10.61
19.50	18.96
1.50	1.96
15.00	14.74
24.00	23.80
6.00	5.75

Figure 9. Mean value of $SO_4^=$ survey 0279 vs. expected values.



x	y
9.10	8.38
28.80	27.42
23.70	22.90
13.10	12.16
7.20	6.77

Figure 10. Mean values of $SO_4^=$ survey 0879 vs. expected values.

TABLE 23. AGENCY APPORTIONMENT OF NITRATE SURVEYS

Agency	Survey 0279, %	Survey 0879, %
ERC (Federal)	1.9	2.3
Regional (Federal)	1.8	2.3
State Agencies	46.3	39.6
Local Agencies	18.5	20.9
Industrial/Contractor	27.8	27.9
Foreign	3.7	7.0

Data Summary

The survey results are listed in Table 24 inclusive of all methods. Results by analytical method are given in Table 25 with the total of unlisted methods included in the "all other" category. Frequency distributions by percent are shown in Table 26. The expected values used in the nitrate surveys were derived from the theoretical amounts of nitrate ion which were deposited on glass fiber filter strips. Chemical composition was verified by corroborative tests carried out by an independent laboratory and by the QAD.

Approximately 7 percent of the measurements were rejected on the basis of independent judgment and Chauvenet's Criterion.

TABLE 24. SUMMARY OF NITRATE PROFICIENCY SURVEYS

Sample no.	Respondents*	Expected value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0279 (February 1979)					
0	50	1.50	1.58	0.41	0.35 - 3.39
1	50	3.60	3.52	0.38	2.53 - 4.60
2	50	5.70	5.52	0.52	4.39 - 7.29
3	50	12.00	11.54	1.32	7.83 - 14.79
4	50	7.80	7.60	0.77	5.04 - 9.16
5	50	9.90	9.68	0.98	7.32 - 13.74
Survey 0879 (August 1979)					
0	40	3.40	3.44	0.44	2.37 - 4.40
2	39	6.00	5.90	0.51	4.22 - 6.88
3	40	10.20	9.97	0.95	7.12 - 11.57
4	40	8.30	7.94	0.84	4.99 - 9.20
5	40	1.20	1.21	0.27	0.36 - 1.82

*With outliers removed.

TABLE 25. NITRATE BY ANALYTICAL METHOD
($\mu g/m^3$)

Sample no.	Expected value	Cadmium reduction-manual N	Mean	Std. dev.	Cadmium reduction-automated N	Mean	Std. dev.	Hydrazine reduction N	Mean	Std. dev.	Hydrazine reduction-automated N	Mean	Std. dev.	All others N	Mean	Std. dev.
Survey 0279* (February 1979)																
0	1.50	3	1.67	0.23	29	1.68	0.87	2	1.68	0.02	5	1.71	0.12	11	1.95	1.92
1	3.60	3	3.38	0.32	29	3.58	1.01	2	3.52	0.32	5	3.73	0.12	11	3.44	0.49
2	5.70	3	5.26	0.68	29	5.61	1.16	2	5.09	0.27	5	5.55	0.34	11	5.77	1.59
3	12.00	3	10.84	1.69	29	11.66	1.98	2	8.78	0.26	5	11.84	0.71	11	11.01	1.42
4	7.80	3	6.88	1.70	29	7.55	1.18	2	6.53	0.18	5	8.15	0.65	11	7.37	0.88
5	9.90	3	8.42	1.11	29	9.50	1.57	2	7.83	0.47	5	8.35	3.64	11	10.01	1.43
Survey 0879* (August 1979)																
0	3.40	4	3.48	0.78	20	3.47	0.30	2	3.14	0.91	3	3.40	0.07	11	3.42	0.53
2	6.00	4	5.31	0.80	19	5.87	0.67	2	6.01	0.59	3	5.72	0.24	11	5.81	0.86
3	10.20	4	9.40	1.70	20	10.24	1.30	2	9.18	0.51	3	10.06	0.25	11	9.92	1.42
4	8.30	4	7.33	1.37	20	8.69	2.47	2	7.91	0.61	3	7.93	0.39	11	7.82	1.14
5	1.20	4	0.99	0.42	20	1.65	1.82	2	1.11	0.55	3	1.06	0.11	11	1.31	0.29

*With outliers removed.

TABLE 26. PERCENT OF NITRATE MEASUREMENTS WITHIN INDICATED PERCENT OF EXPECTED VALUE

Survey 0279					Survey 0879				
Sample No.	10%	20%	30%	50%	Sample No.	10%	20%	30%	50%
0	52	74	82	88	0	55	88	98	100
1	72	90	96	96	2	79	89	95	100
2	74	88	94	94	3	75	90	93	100
3	74	86	96	98	4	80	93	93	98
4	78	94	96	98	5	55	70	83	93
5	78	90	94	96					

The mean values from survey 0279, plotted against the expected values, gave a linear relationship, as follows:

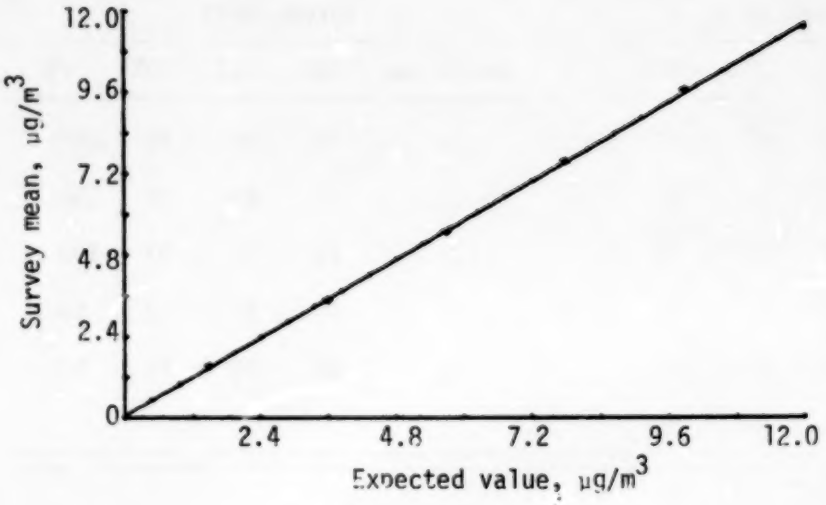
Survey average = 0.1117 + 0.9573 (expected value)
R^2 = 0.9998

A plot of the survey means (y) against the expected values (x) is shown in Figure 11.

The mean values from survey 0879, plotted against the expected values, gave a linear relationship, as follows:

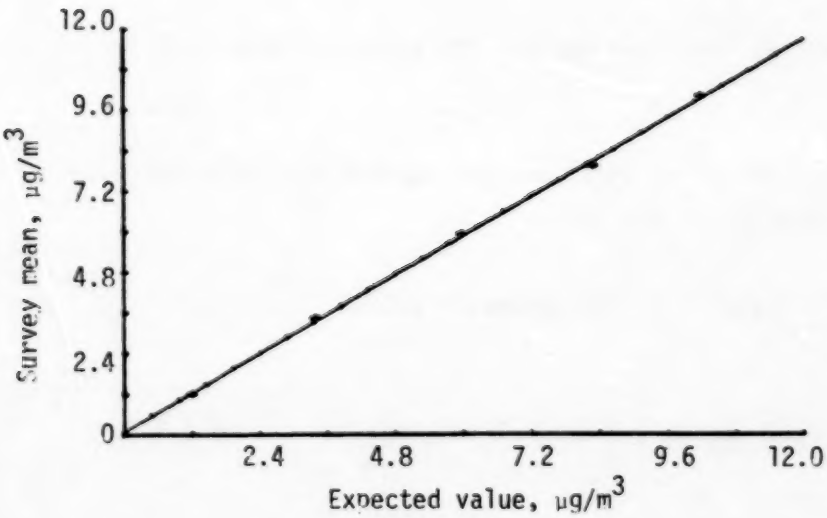
Survey average = 0.1002 + 0.9608 (expected value)
R^2 = 0.9994

A plot of the survey means (y) against the expected values (x) is shown in Figure 12.



x	y
1.50	1.58
3.60	3.52
5.70	5.52
12.00	11.54
7.80	7.60
9.90	9.68

Figure 11. Mean values of NO_3^- survey 0279 vs. expected values.



x	y
3.40	3.44
6.00	5.90
10.20	9.97
8.30	7.94
1.20	1.21

Figure 12. Mean values of NO_3^- survey 0879 vs. expected values

Summary

Proficiency Surveys for NO_3^- were completed by approximately 45 participants in February and August 1979. The predominant test method was the automated cadmium reduction procedure, used by over half the respondents. In all, nine analytical methods were reported in use. No method was particularly bad and no systematic discrepancies existed.

LEAD

Test Method

Virtually all participants in both the 0179 and 0779 surveys employed the atomic absorption analytical method as they did in previous years. Only one participant reported using another method, the anodic stripping voltmeter method.

Agency Apportionment

State and local agencies taking part in the lead survey together decreased by 17 percent while participation of private industry increased by 12 percent from the previous year.[7] The categories of agencies which were involved in the lead surveys are listed in Table 27.

TABLE 27. AGENCY APPORTIONMENT OF LEAD SURVEYS

Agency	Survey 0179, %	Survey 0779, %
ERC (Federal)	1.3	0.0
Regional (Federal)	7.9	6.9
State Agencies	47.4	44.8
Local Agencies	25.0	25.3
Industrial/Contractor	17.1	19.5
CAMP	1.3	1.2
Foreign	0.0	2.3

Data Summary

The survey results are tabulated in Table 28. Results by analytical method are summarized in Table 29. Frequency distributions of the percent of the expected value are shown in Table 30. The expected values used in the lead survey were designated after considering the results of corroborative analyses.

Anomolous measurements are not included in the summary tables. Judgment and Chauvenet's Criterion were used to reject approximately 1 percent of the measurements in the 0179 survey and 8 percent in the 0779 test.

TABLE 28. SUMMARY OF LEAD PROFICIENCY SURVEYS

Sample no.	Respondents*	Expected value $\mu g/m^3$	Survey mean $\mu g/m^3$	Survey std. dev. $\mu g/m^3$	Survey interval $\mu g/m^3$
Survey 0179 (January 1979)					
3	76	1.46	1.45	0.16	0.93 - 1.95
4	76	3.52	3.46	0.28	2.84 - 4.32
5	76	5.39	5.39	0.57	2.88 - 6.63
6	76	11.45	11.31	1.15	7.74 - 14.10
7	76	7.48	7.61	1.10	4.80 - 12.00
8	76	9.51	9.38	0.96	6.18 - 11.57
Survey 0779 (July 1979)					
0	81	3.53	3.53	0.29	2.34 - 4.20
1	81	12.86	12.85	0.87	10.59 - 15.30
2	79	5.85	5.90	0.34	4.77 - 6.97
3	81	10.39	10.42	0.91	7.50 - 13.80
4	80	7.93	7.99	0.48	6.81 - 9.97
5	81	1.18	1.17	0.12	0.84 - 1.50

*With outliers removed.

TABLE 29. LEAD BY ANALYTICAL METHOD
($\mu g/m^3$)

Sample no.	Atomic absorption			All others		
	N	Mean	Std. dev.	N	Mean	Std. dev.
Survey 0179* (January 1979)						
3	75	1.48	0.24	1	1.30	0.00
4	75	3.49	0.50	1	3.20	0.00
5	75	5.50	1.15	1	5.10	0.00
6	75	11.19	1.48	1	10.60	0.00
7	75	7.71	1.68	1	7.00	0.00
8	75	9.42	1.72	1	8.70	0.00
Survey 0779* (July 1979)						
0	81	3.53	0.29			
1	81	12.85	0.87			
2	79	5.90	0.34			
4	80	7.99	0.48			
5	81	1.17	0.12			
3	81	10.42	0.91			

*Outliers removed.

TABLE 30. PERCENT OF LEAD MEASUREMENTS WITHIN INDICATED PERCENT OF EXPECTED VALUE

Survey 0179					Survey 0779				
Sample No.	10%	20%	30%	50%	Sample No.	10%	20%	30%	50%
3	74	92	95	99	0	85	98	99	100
4	79	97	99	99	1	89	100	100	100
5	76	91	96	97	2	92	100	100	100
6	78	91	97	99	3	86	95	98	100
7	76	91	92	93	4	95	98	99	100
8	70	93	97	99	5	74	100	100	100

The mean values from survey 0179, plotted against the expected values, gave a linear relationship, as follows:

Survey average = 0.0328 + 0.9895 (expected values)
R^2 = 0.9994

A plot of the survey means (y) against the expected values (x) is shown in Figure 13.

The mean values from survey 0779, plotted against the expected values, gave a linear relationship, as follows:

Survey average = 0.0122 + 1.0011 (expected value)
R^2 = 1.0000

A plot of the survey 0779 means (y) against the expected values (x) is shown in Figure 14.

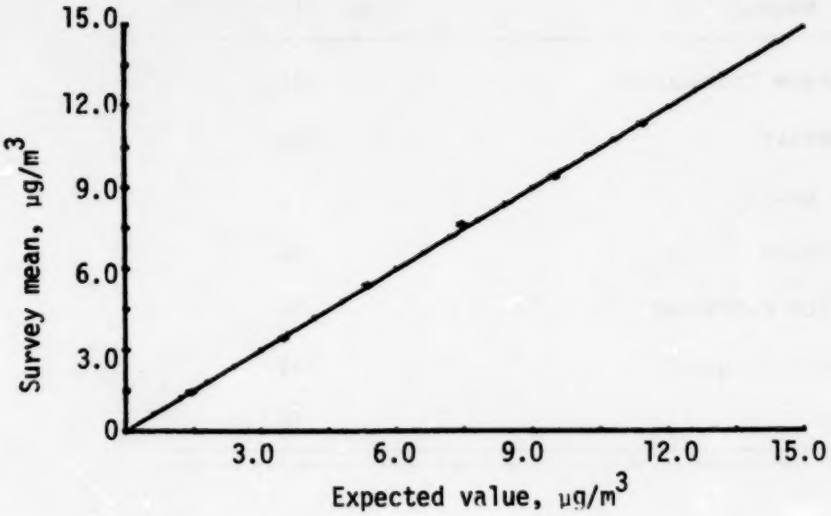
Summary

Proficiency Surveys for Pb were conducted in January and July 1979, with approximately 80 facilities participating. The atomic absorption method of analysis was virtually the only method used. No systematic discrepancies or bias was observed in the Pb surveys.

HI-VOL FLOW

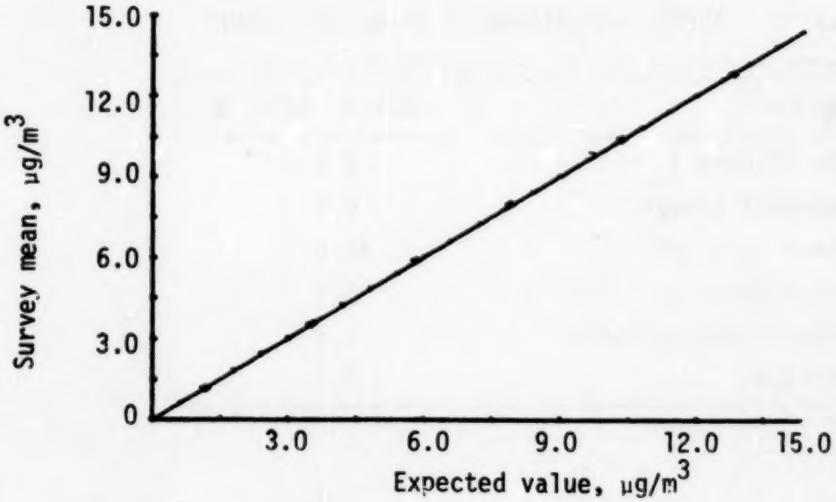
Test Method

Six measurement methods were listed by survey participants. The pressure transducer and rotameter dominated with 72.6 percent using those methods. Other minor methods, as noted on the survey information forms, were flow gauge, manometer, orifice manometer, and magnehelic gauge. Five percent of the methodologies were not reported. The categories of the various methods, together with a summary of sites, is given in Table 31.



x	y
1.46	1.45
3.52	3.46
5.39	5.39
11.45	11.31
7.48	7.61
9.51	9.38

Figure 13. Mean values of Pb survey 0179 vs. expected values



x	y
3.53	3.53
12.86	12.85
5.85	5.90
10.39	10.42
7.93	7.99
1.18	1.17

Figure 14. Means of Pb survey 0779 vs. expected values

TABLE 31. ANALYTICAL METHODS - HI-VOL

Method	No. of sites
Pressure transducer	546
Rotameter	496
Flow gauge	72
Manometer	56
Orifice manometer	36
Magnehelic gauge	34
Other	58

Agency Apportionment

The number of air monitoring offices taking part in the 0579 survey and the distribution of agencies remained close to the same as the previous year[7]. The division of agencies is shown in Table 32.

TABLE 32. AGENCY APPORTIONMENT OF HI-VOL SURVEY

Agency	Survey 0579, %
ERC (Federal)	0.3
Regional (Federal)	0.8
State Agencies	40.6
Local Agencies	53.9
Industrial/Contractor	1.8
Foreign	2.6

Data Summary

It was not practical to furnish standardized ReF specimens from an invariant population of samples. Each sample ReF unit was calibrated individually and is distinct from all other units, in as much as flow rates could not be duplicated precisely enough among the test devices to establish flow values that were applicable to all units. Rather than comparing collective measurements against a common standard, results from each ReF are compared to a calibration which is unique for that unit. The calibrated flow values, or expected values, developed for each of five flow constrictor plates, are compared to the values recorded on the survey forms. To facilitate the comparison, the expected values are termed "x" and the reported values are referred to as "y". The five x, y pairs are plotted to obtain a linear regression plot, with the expectation that the coefficient of linearity (r) should be 1, the slope should be 1, and the y intercept should pass through the x, y origin. Departures from this norm are due to any single or combination of defects that falsify the measured flow. Three categories of measurements were evaluated--data obtained by use of a pressure transducer, those obtained by a rotameter and those from all methods combined together. A substantial part of the measurements fall in the "all other" category. Table 31 makes reference to the secondary methods that were used. The linear regression equations of the three categories are given in Table 33.

TABLE 33. LINEAR REGRESSION EQUATIONS OF PAIRED VALUES

All Methods:	$y = 0.925x + 3.560$	(9)
Pressure transducer:	$y = 0.943x + 2.498$	(10)
Rotameter:	$y = 0.907x + 4.696$	(11)

where: y = reported value, cu. ft./min.
x = expected value, cu. ft./min.

Frequency distributions of the percent differences between the reported and expected values for each measurement pair are shown in Table 34.

TABLE 34. PERCENT DIFFERENCE FROM EXPECTED FLOW

Number of Measurements*	Percent of Measurements					
	10%	20%	30%	50%	70%	90%
5902	-9.2	-4.8	-2.6	0.3	3.0	7.4

*With outliers removed.

Summary

The Proficiency Survey for hi-vol flow was conducted in May 1979 with approximately 1,300 sites being tested. Foreign, federal, state and industrial laboratories participated in the testing program. The pressure transducer and rotameter were the most common methods used with four other minor methods. A slight bias existed in the major methods and in the data from all methods combined.

SECTION 6
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